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# Collaborative Testing of EOA Method 106 (Vinyl Chloride) that will Provide for a Standardized Stationary Source Emission Measurement Method

Midwest Research Inst, Kansas City, MO

Prepared for

Environmental Monitoring and Support Lab, Research Triangle Park, NC

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Research Triangle Park NC 27711

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# Collaborative Testing of EPA Method 106 (Vinyl Chloride) that Will Provide for a Standardized Stationary Source Emission Measurement Method

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Method 106 - Determination of Vinyl Chloride from Stationary Sources was evaluated in a two-part collaborative test. Gaseous samples, prepared in cylinders and containing interferences in some cases, were analyzed by a group of 10 collaborators. The results showed that Chromosorb 102/SF-96 columns performed better when acetaldehyde interference was present, but Chromosorb 102 alone was better when isobutane interference was present. Collaborator biases averaged 0.18 ppm (0.47 $mg/m^3$) low with a standard deviation of 0.72 ppm (1.86 $mg/m^3$). Both peak height and area measurements yielded similar results and the bias found was due entirely to low results from using Chromosorb 102 and not from the Chromosorb 102/SF-96 column.

A three collaborator field test was conducted on the vent of a carbon bed absorber at a vinyl chloride polymer facility. The group had a standard deviation of 0.39 ppm (1.01 $mg/m^3$) and 0.24 ppm (0.62 $mg/m^3$) for sampling and analysis, respectively. Analyst skill is a major factor in the use of Method 106.

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# COLLABORATIVE TESTING OF EPA METHOD 106 (VINYL CHLORIDE) THAT WILL PROVIDE FOR A STANDARDIZED STATIONARY SOURCE EMISSION MEASUREMENT METHOD

by

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FINAL REPORT

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i.a.

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## FOREWORD

Midwest Research Institute, under EPA Contract No. 68-02-2737, conducted collaborative tests of Method 106, "Determination of Vinyl Chloride from Stationary Sources." A group of 10 collaborators at their own laboratories analyzed six simulated samples containing vinyl chloride and interferring compounds. Three laboratories then obtained field samples and analyzed the samples. This report describes the collaborative tests and includes statistical analyses of the test results.

Approved for:

MIDWEST RESEARCH INSTITUTE

L. J. Shannon, Director
Environmental and Materials
Sciences Division

October 1978

## ABSTRACT

A two-part collaborative test was conducted for Method 106, "Determination of Vinyl Chloride from Stationary Sources." A group of 10 collaborators analyzed a set of synthetic samples, some of which contained interferences, for vinyl chloride. Analytical results were reported by peak height and by peak area. All samples were analyzed on both 2m Chromosorb 102 and 2m Chromosorb 102/2m SF-96 columns. Most of the collaborators correctly identified the vinyl chloride peaks. Chromosorb 102/SF-96 performed better in the presence of acetaldehyde and Chromosorb 102 alone was better for isobutane interferences. In all cases the chromatograms showed proper responses. The errors that were made were due to interpretation of the results. The skill of the analyst is a major factor in the use of Method 106. The collaborators obtained values which averaged 0.18 ppm (0.47 $mg/m^3$) low with a standard deviation of 0.72 ppm (1.86 $mg/m^3$). There was no overall superiority noted for peak height versus area. The bias found was entirely due to low results using only Chromosorb 102. Chromosorb 102/SF-96 gave a bias that was 0.01 ppm (0.03 $mg/m^3$) low.

A field test of the method was then conducted by three groups on the vent from a carbon bed adsorber. The group of collaborators had a standard deviation of 0.46 ppm (1.19 $mg/m^3$) for sampling and analysis combined. The standard deviation for sampling from the same source was 0.39 ppm (1.01 $mg/m^3$) and 0.24 ppm (0.62 $mg/m^3$) for the analysis of the samples obtained. A brief comparison of a charcoal adsorption tube method gave results which were about 20% lower than results obtained using Method 106.



This report was submitted in fulfillment of Contract No. 68-02-2737 by Midwest Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 1977 to April 1978, and work was completed as of May 1978.

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# SECTION 1

## INTRODUCTION

On December 24, 1975, under Section 112 of the Clean Air Act, as amended, the Environmental Protection Agency (EPA) added vinyl chloride to the list of hazardous air pollutants[1] because it has been implicated as the causal agent of angiosarcoma and other serious disorders. A national emission standard has been promulgated[2] that covers plants that manufacture ethylene dichloride, vinyl chloride, and polyvinyl chloride. These regulations include a method for determining vinyl chloride emissions from stationary sources, EPA Method 106. The Quality Assurance Branch of the Environmental Monitoring and Support Laboratory at Research Triangle Park, North Carolina, has as its task the evaluation and standardization of EPA source test methods. While participating in this program, Midwest Research Institute (MRI) has undertaken a collaborative test of EPA Method 106.

The objective of this project was to conduct a collaborative test of EPA Reference Method 106 (vinyl chloride). A collaborative test is a procedure in which a group of persons from different laboratories conduct sampling and analysis under identical conditions using the same method. It provides information on the variability of method results between laboratories as well as the reproducibility of a single analyst's results. A properly designed collaborative test should demonstrate the reliability of the method being tested under typical, realistic sampling and analysis conditions.

The first goal under this program was to contact potential collaborators and determine their experience in gas chromatographic analysis and vinyl chloride sampling techniques.

Following the evaluation of potential collaborators, 10 participants were selected for the collaborative tests. Each collaborator was supplied with six samples for analysis. The samples consisted of a minimum of four levels of vinyl chloride with at least two samples containing organic compounds that are potential interferences. The samples were obtained from a reputable gas supplier who ascertained that the samples were stable and of the correct concentration.

MRI analyzed one set of samples at periodic intervals during the duration of the collaborative test. MRI also sent one set of samples to the National Bureau of Standards (NBS) for certification of the stated concentrations.

A source of vinyl chloride emission at or below 15 ppm (40 $mg/m^3$) was located by MRI. Arrangements were made for three collaborators to obtain replicate and simultaneous samples from the selected source using Method 106. The collected samples were analyzed within 24 hr after collection. Samples were also collected using a charcoal tube absorption technique.

At the conclusion of the laboratory and field collaborative test of Method 106, MRI statistically evaluated the analytical results.

The following sections of this report include the results and statistical analyses of the collaborative tests. General conclusions and recommendations obtained from the study are also presented.

## SECTION 2

## CONCLUSIONS

The major conclusions obtained from the collaborative tests are:

1. For vinyl chloride concentrations < 10 ppm (25 mg/$m^3$), a collaborator has a repeatability of $\pm$ 0.5 ppm (1.3 mg/$m^3$) or better, but at 50 ppm (125 mg/$m^3$) vinyl chloride this value is much larger ($\sim \pm$ 6 ppm, 15 mg/$m^3$).

2. A set of collaborators will read a given low concentration vinyl chloride sample to within approximately $\pm$ 1.25 ppm (3 mg/$m^3$) (except at 50 ppm (125 mg/$m^3$) vinyl chloride it becomes $\pm$ 10 ppm, 25 mg/$m^3$).

3. The physical sample-sample contribution to collaborator variation is comparable to the analytical contribution.

4. The biasses exhibited are on the order of -0.1 ppm (0.3 mg/$m^3$) for pure vinyl chloride and -0.2 ppm (0.5 mg/$m^3$) for interferred vinyl chloride, when reliable readings are produced. However, one (of 10) collaborator was fooled by all interferences, and the set of collaborators failed to produce reliable observations 40% of the time on the 45.1 ppm (82 mg/$m^3$) acetaldehyde sample.

5. There is no distinction between height and area methods. The Chromosorb 102/SF-96 measurements are unbiased, and therefore are to be preferred, statistically, to the negatively biased Chromosorb 102 measurements. The Chromosorb 102 bias ($\sim$ -0.3 ppm, 0.8 mg/$m^3$), is, however, small compared to the repeatibility contributions.

6. The charcoal adsorption tube allows a much simplified sampling procedure compared to Method 106 but the analysis procedure is more difficult and not as accurate.

## SECTION 3

## RECOMMENDATIONS

Based upon the conclusions that have been obtained from this collaborative test, it is recommended that:

1. Method 106 continue to be used in its present form as an acceptable method for the analysis of vinyl chloride from stationary sources.

2. Further consideration be given to determining the equivalence of Method 106 and a charcoal adsorption tube method.

## SECTION 4

## SELECTION OF COLLABORATORS

A letter, which is shown in Appendix A, was sent to approximately 80 organizations to determine their interest and qualification for participating in the collaborative test. Fifteen potentially qualified collaborators responded with bids. All 15 collaborators were considered technically acceptable. The 10 firms submitting the lowest bids were therefore selected. The collaborators are:

Dr. Douglas S. Kendall
Commercial Testing and Engineering Company
14335 West 44th Avenue
Golden, Colorado 80401
Analyst: Dr. Douglas S. Kendall

Dr. Perry Lonnes
Interpoll, Inc.
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Analyst: Dr. Joseph D. Banzer

Dr. David C. Kennedy
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Mr. Robert D. Soule, P.E.
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Analyst: Mr. Kent Shoemaker

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Mr. Arthur Engelmen
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Analyst: Mr. Michael Oliverio

Dr. Gene Dennison
Envirotest Laboratories
103 East Prospect Street
Hopewell, New Jersey 08525
Analyst: Mr. Robert Menichelli

Mr. Bernard J. DeWitt
PPG Industries, Inc.
P.O. Box 31
Barberton, Ohio 44203
Analyst: Mr. James Hendershott

## SECTION 5

## COLLABORATIVE TEST DESIGN

Six different gas mixtures were prepared by Scott Specialty Gases for the laboratory collaborative test. Twelve sets of these mixtures were then made using 200 liter capacity low pressure cylinders. One set was for stability checks by MRI. One set was shipped to the NBS to obtain reference values of vinyl chloride assigned. Each collaborator would receive one of the remaining 10 sets.

Each collaborator analyzed each sample according to the instructions given in Appendix B using the current version of Method 106 with amendments (Federal Register, Vol. 41, pp. 46569-46571, October 21, 1976; amended Vol. 42, pp. 29007-29009, June 7, 1977) given in Appendix C. Each collaborator reported both peak height and peak area results for both the 2m Chromosorb 102 column and for the 2m Chromosorb 102/2m SF-96 column combination. Thus, systematic differences in the methods were measurable.

The approximate compositions of the samples were:

1. 5 $mg/m^3$ (2 ppm) vinyl chloride

2. 20 $mg/m^3$ (8 ppm) vinyl chloride

3. 18 $mg/m^3$ (7 ppm) vinyl chloride and 80 $mg/m^3$ (50 ppm) acetaldehyde

4. 30 $mg/m^3$ (12 ppm) vinyl chloride, 15 $mg/m^3$ (10 ppm) methanol, and 50 $mg/m^3$ (20 ppm) isobutane

5. 18 $mg/m^3$ (7 ppm) vinyl chloride, 7 $mg/m^3$ (5 ppm) methanol, and 25 $mg/m^3$ (10 ppm) isobutane

6. 30 $mg/m^3$ (20 ppm) acetaldehyde

All samples have nitrogen as the balance gas.

Samples 1 and 2 measure the accuracy of each collaborator's calibration gases. Sample 3 is a mixture which should be difficult to resolve on Chromosorb 102, but easy on the combined columns. Samples 4 and 5 are similar and should be easier to resolve on Chromosorb 102. Sample 6 contains no vinyl chloride and indicates the skill of the analyst's recognizing a false vinyl chloride peak.

## SECTION 6

## LABORATORY COLLABORATIVE TEST RESULTS

The samples were prepared, aged, and checked for vinyl chloride stability. They were then shipped to MRI. One set of cylinders was chosen at random and the first analysis of the samples was completed by MRI on September 12. After verifying that each mixture could be measured on at least one of the columns, the collaborators' samples were shipped. One set was also shipped to NBS.

Tables 1 and 2 summarize the results of the test. The tables include analysis results by Scott, NBS, MRI, and the collaborators. Collaborator D did not submit results until 4 months after the samples were shipped. All other collaborators completed their analyses within the 1-month period allowed. Since Collaborator D submitted results which demonstrated no obvious anomalies, their results are included in the final data set. Vinyl chloride in cylinders is normally stable for periods of more than 1 year without detectable changes in concentration. The only component which is unstable is acetaldehyde and it was still clearly present in Collaborator D's chromatograms.

Collaborators B and F found no acetaldehyde peaks in their samples. The suspect cylinders were returned to MRI. Acetaldehyde was clearly detected in all of the suspect samples by MRI. Neither collaborator has been able to suggest any reason for the loss of acetaldehyde on a Chromosorb 102 column.

However, acetaldehyde is irreversibly retained by many polar materials in addition to an SF-96 column. In many instances the collaborators reported suspect values which they rejected due to the probable presence of interferences. Collaborators E, G, and K did not indicate that Sample 10673 was not vinyl chloride. An examination of these data by MRI indicates that the differences in retention time should have been sufficient to reject the peaks as not vinyl chloride.

MRI conducted two analyses of the samples 1 month apart. As the data in Tables 1 and 2 indicates, the samples were all stable. Samples 60106 and 4786 were pure vinyl chloride. Both columns performed equally well. Samples 4036 and 6800 are similar. On Chromosorb 102, two peaks are seen incompletely

# TABLE 1. COLLABORATORS' VINYL CHLORIDE ANALYSIS RESULTS ($mg/m^3$)

| | SRI ($mg/m^3$) | Collaborator A | Collaborator B[a] | Collaborator C | Collaborator D[a] | Collaborator E | Collaborator F | Collaborator G | Collaborator H | Collaborator J | Collaborator K | MRI Sept. 12 | MRI Oct. 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1814 (17.6 $mg/m^3$ vinyl chloride, 82 $mg/m^3$ acetaldehyde) | 17.5 | | | | | | | | | | | | |
| Chromosorb 102 height | | 73.3[c] | 12.4 | 43.8[c,e] | g/ | 28.0[c] | 15.3 | 50.71 | 37.8[c] | 24.9[c] | 16.8 | 20.5 | 9.1 |
| Chromosorb 102 area | | 19.8[c] | 12.6 | 48.6[c] | 31.78[c] | 42.2[c] | 15.3 | 52.78[d] | 72.0[c] | 48.2[c] | 16.1 | 35.5 | g/ |
| Chromosorb 102 and SF-96 height | | 17.2 | 15.3 | 18.6 | 15.4 | 14.2 | 14.5 | 17.4 | 18.4 | 15.8 | 20.7 | 16.3 | 16.6 |
| Chromosorb 102 and SF-96 area | | Not Measurable[c] | 15.8 | 17.9 | 18.0 | 19.9[c] | 16.1 | 17.2 | 18.2 | 15.5 | 20.2 | 16.6[d] | 17.1[d] |
| 5036 (33.7 $mg/m^3$ vinyl chloride, 9.4 $mg/m^3$ methanol, 31 $mg/m^3$ isobutane) | 33.7 | | | | | | | | | | | | |
| Chromosorb 102 height | | 28.7 | 34.9 | 35.5 | 34.45 | 32.4 | 31.6 | 33.18 | 34.58 | 33.4 | 119 | 28.2 | 31.1 |
| Chromosorb 102 area | | 28.2 | 34.3 | 36.0 | 35.91 | 31.1 | 30.3 | 33.6[d] | 33.33 | 33.4 | 155 | 30.1[c] | 32.6[d] |
| Chromosorb 102 and SF-96 height | | 32.9 | 30.0 | 34.7 | 34.60 | 33.4[c] | 31.3 | 34.36 | 34.24 | 29.1[c] | 106 | 36.5 | g/ |
| Chromosorb 102 and SF-96 area | | 32.9 | 31.6 | 35.0 | 34.40 | 34.2[c] | 30.0 | 34.36 | 32.9 | 28.2[c] | 150 | g/ | g/ |
| 6800 (18.2 $mg/m^3$ vinyl chloride, 6.0 $mg/m^3$ methanol, 25.5 $mg/m^3$ isobutane) | 19.0 | | | | | | | | | | | | |
| Chromosorb 102 height | | 16.6 | 15.3 | 19.7 | 19.40 | 20.5 | 17.6 | 18.9 | 20.0 | 18.6 | 60 | 16.6 | 17.4 |
| Chromosorb 102 area | | 16.1 | 15.5 | 21.8 | 19.45 | 20.5 | 16.8 | 18.9[d] | 19.7 | 18.4 | 83 | 17.6[d] | 17.6 |
| Chromosorb 102 and SF-96 height | | 18.9 | 16.8 | 20.7 | 19.45 | 19.9[c] | 16.8 | 18.3 | 19.7 | 19.4 | 80 | 20.5 | g/ |
| Chromosorb 102 and SF-96 area | | 18.7 | 17.6 | 19.7 | 19.32 | 22.3[c] | 16.8 | 18.4 | 18.9 | 19.2 | 78 | g/ | g/ |
| 10673 (34 $mg/m^3$ acetaldehyde) | < 0.11 | | | | | | | | | | | | |
| Chromosorb 102 height | | 35.0[c] | n.d. | 10.1[c] | n.d. | 19.7 | n.d. | 12.2 | 3.57[c] | n.d. | 1.3 | Wrong retention time- | |
| Chromosorb 102 area | | 17.1[c] | n.d. | 11.1[c] | n.d. | 19.4 | n.d. | 13.0[d] | 6.9[c] | n.d. | 1.3 | not vinyl chloride | |
| Chromosorb 102 and SF-96 height | | n.d. | n.d. | n.d. | n.d. | 7.1[c] | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Chromosorb 102 and SF-96 area | | n.d. | n.d. | n.d. | n.d. | 22.1[c] | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 5786 (22.6 $mg/m^3$ vinyl chloride) | 22.2 | | | | | | | | | | | | |
| Chromosorb 102 height | | 19.1 | 16.1 | 21.1 | 21.9 | 22.5 | 20.2 | 21.7 | 22.9 | 21.0 | 22.3 | 20.2 | 20.7 |
| Chromosorb 102 area | | 18.8 | 17.1 | 21.8 | 23.5 | 22.0 | 20.2 | 21.6[d] | 22.9 | 21.0 | 21.8 | 19.7[d] | 20.7[d] |
| Chromosorb 102 and SF-96 height | | 23.2 | 19.3 | 21.8 | 22.7 | 23.8 | 19.4 | 22.7 | 22.9 | 19.7[c] | 24.9 | 20.5 | 20.7 |
| Chromosorb 102 and SF-96 area | | 22.6 | 19.9 | 23.1 | 22.9 | 23.1 | 20.5 | 22.4 | 23.0 | 19.8[c] | 25.4 | 20.3[d] | 21.2[d] |
| 60108 (5.80 $mg/m^3$ vinyl chloride) | 5.83 | | | | | | | | | | | | |
| Chromosorb 102 height | | 6.89 | 5.9 | 6.0 | 5.62 | 6.0 | 6.5 | 5.62 | 7.23 | 5.7 | 6.2 | 5.08 | 5.31 |
| Chromosorb 102 area | | 6.71 | 6.1 | 7.1 | 6.01 | 5.7 | 6.7 | 5.78[d] | 6.89 | 5.5 | 6.2 | 5.39[d] | 5.31[d] |
| Chromosorb 102 and SF-96 height | | 5.19 | 6.7 | 6.7 | 6.11 | 6.2 | 5.4 | 6.40 | 7.23 | 5.7 | 6.5 | 5.46 | 5.49 |
| Chromosorb 102 and SF-96 area | | 5.05 | 6.0 | 6.2 | 5.80 | 7.0 | 6.9 | 6.58 | 6.89 | 5.. | 7.3 | 5.31[d] | 5.5[d] |

a/ Data received late.

b/ Data corrected for revised analyses in vinyl chloride standards as reported by supplier.

c/ Instrument malfunction; not able to obtain reading.

d/ Best value.

e/ Interference suspected--result reported by collaborator.

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# TABLE 2. COLLABORATORS' VINYL CHLORIDE ANALYSIS RESULTS (PPM)

| | SRS (ppm) | Collaborator A | Collaborator B[1] | Collaborator C | Collaborator D[2] | Collaborator E | Collaborator F | Collaborator G | Collaborator H | Collaborator J | Collaborator K | MRI Sept. 1[1] | MRI Oct. 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1B1; (6.8 ppm vinyl chloride, 40.1 ppm acetaldehyde) | 6.75 | | | | | | | | | | | | |
| Chromosorb 102 height | | 25.0[3] | 5.8 | 16.9[3] | x[4] | 10.8[3] | 5.9 | 19.58 | 14.6[3] | 9.5[3] | 6.5 | 7.4 | 5.5 |
| Chromosorb 102 area | 7% | 7.1[3] | 5.8 | 18.7[3] | 12.27[3] | 16.3[3] | 5.9 | 20.36[3] | 27.8[3] | 18.6[3] | 6.2 | 13.7 | x[4] |
| Chromosorb 102 and SP-96 height | | 6.66 | 5.9 | 7.2 | 5.94 | 5.5 | 5.6 | 6.71 | 7.11 | 6.1 | 8.0 | 6.3 | 6.4 |
| Chromosorb 102 and SP-96 area | | Not measurable[4] | 6.1 | 6.9 | 6.95 | 15.4[3] | 6.2 | 6.66 | 7.04 | 6.0 | 7.8 | 6.4[5] | 6.6[5] |
| 2B1; (11.0 ppm vinyl chloride, 7.1 ppm methanol, 21.1 ppm isobutane) | 11.0 | | | | | | | | | | | | |
| Chromosorb 102 height | | 11.1 | 9.6 | 14.7 | 13.30 | 12.5 | 12.2 | 12.81 | 13.35 | 12.9 | 46 | 10.9 | 12.0 |
| Chromosorb 102 area | | 10.9 | 9.6 | 13.9 | 13.68 | 12.0 | 11.7 | 12.85[3] | 12.87 | 12.9 | 60 | 11.7[5] | 12.5[5] |
| Chromosorb 102 and SP-96 height | | 12.7 | 11.6 | 13.6 | 13.36 | 12.9[3] | 12.1 | 13.26 | 13.22 | 11.3[3] | 41 | 14.1 | x[4] |
| Chromosorb 102 and SP-96 area | | 12.7 | 12.2 | 13.5 | 13.28 | 13.2[3] | 11.6 | 13.26 | 12.7 | 11.1[3] | 58 | x[4] | x[4] |
| 3B1; (7.9% ppm vinyl chloride, 6.3 ppm methanol, 10.8 ppm isobutane) | 7.3 | | | | | | | | | | | | |
| Chromosorb 102 height | | 8.3 | 5.9 | 7.6 | 7.49 | 7.9 | 6.8 | 7.29 | 7.71 | 7.2 | 23 | 6.4 | 6.7 |
| Chromosorb 102 area | | 8.21 | 6.0 | 8.4 | 7.31 | 7.9 | 6.5 | 7.28[3] | 7.62 | 7.1 | 32 | 6.8[5] | 6.8 |
| Chromosorb 102 and SP-96 height | | 7.91 | 6.5 | 8.0 | 7.51 | 7.7[3] | 6.5 | 7.08 | 7.60 | 7.5 | 31 | 7.9 | x[4] |
| Chromosorb 102 and SP-96 area | | 7.22 | 6.8 | 7.6 | 7.46 | 8 6[3] | 6.5 | 7.12 | 7.30 | 7.4 | 30 | x[4] | x[4] |
| 1B2; (18.4 ppm acetaldehyde) | <0.05 | | | | | | | | | | | | |
| Chromosorb 102 height | | 11.0[3] | n.d. | 3.9[3] | n.d. | 7.6 | n.d. | 4.72 | 1.38[3] | n.d. | 0.5 | Wrong retention time- not vinyl chloride | |
| Chromosorb 102 area | | 17.6[3] | n.d. | 6.1[3] | n.d. | 7.5 | n.d. | 5.05[3] | 2.67[3] | n.d. | 0.5 | | |
| Chromosorb 102 and SP-96 height | | n.d. | n.d. | n.d. | n.d. | 2.8[3] | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Chromosorb 102 and SP-96 area | | n.d. | n.d. | n.d. | n.d. | 8.6[3] | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 4B2; (8.73 ppm vinyl chloride) | 8.57 | | | | | | | | | | | | |
| Chromosorb 102 height | | 7.38 | 7.5 | 9.0 | 8.47 | 8.7 | 7.8 | 8.37 | 8.86 | 8.1 | 8.6 | 7.8[5] | 8.0 |
| Chromosorb 102 area | | 7.27 | 6.5 | 9.2 | 9.06 | 8.5 | 7.8 | 8.42[3] | 8.84 | 8.1 | 8.4 | 7.6[5] | 8.0[5] |
| Chromosorb 102 and SP-96 height | | 8.95 | 7.6 | 9.2 | 8.77 | 9.2 | 7.5 | 8.77 | 8.85 | 7.6[3] | 9.6 | 7.9 | 8.6 |
| Chromosorb 102 and SP-96 area | | 8.73 | 7.7 | 8.9 | 8.85 | 8.9 | 7.9 | 8.66 | 8.87 | 7.5[3] | 9.8 | 7.9[5] | 8.2[5] |
| 5B1; (2.1% ppm vinyl chloride) | 2.25 | | | | | | | | | | | | |
| Chromosorb 102 height | | 1.8[3] | 1.7 | 2.3 | 2.17 | 2.3 | 2.5 | 2.17 | 2.79 | 2.2 | 2.4 | 1.96 | 2.05 |
| Chromosorb 102 area | | 1.82 | 1.6 | 2.9 | 2.32 | 2.2 | 1.8 | 2.23[3] | 2.66 | 2.1 | 2.4 | 2.08 | 2.05[5] |
| Chromosorb 102 and SP-96 height | | 2.08 | 1.8 | 2.6 | 2.36 | 2.4 | 2.1 | 2.47 | 2.79 | 2.2 | 2.5 | 2.11 | 2.12 |
| Chromosorb 102 and SP-96 area | | 1.91 | 2.1 | 2.4 | 2.24 | 2.7 | 1.9 | 2.50 | 2.66 | 2.1 | 2.8 | 2.05[5] | 2.14[5] |

1/ Data received late.

2/ Data corrected for revised analyses in vinyl chloride standards as reported by supplier.

3/ Instrument malfunctioned; not able to obtain reading.

4/ Best value.

5/ Interference suspected--result rejected by collaborator.



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separated but sufficient to accurately measure both height and area. On the combined columns, vinyl chloride becomes a slight shoulder on the leading edge of the interference peak. The peak height can be estimated but no information on peak area is obtainable without complex peak shape analyses. Apparently, the methanol peak has shifted and merged with the isobutane peak. Sample 10673, acetaldehyde only, shows normal peak shape but with a retention time of about 0.3 min shifted on Chromosorb 102. On the combined columns no peaks are detectable indicating permanent retention of acetaldehyde by the SF-96 column. Sample 1814, vinyl chloride and acetaldehyde, shows a single peak with nearly double normal peak width on Chromosorb 102. On the combined columns only a single normal peak is present at the vinyl chloride retention time. The values measured by MRI are slightly lower than those reported by Scott, but may be due to small errors in the last comparison against permeation tube standards.

## SECTION 7

## STATISTICAL ANALYSIS - LABORATORY TEST

Structurally, this data set is a 6 (levels of vinyl chloride (VC)) x 10 (collaborators) x 4 (methods) factorial analysis of variance (AOV). The primary objective of the analysis is to estimate the components of variance, namely:

$\sigma_e^2$ = The variance of repeated measurements by a single collaborator at a fixed level of VC.

$\sigma_c^2$ = The variance of VC measurements between collaborators (over and above that which would arise due strictly to $\sigma_e^2$).

$\sigma_m^2$ = The variance of VC measurements due to method-method differences.*

$\sigma_L^2$ = The variance due to level-level differences.

$\sigma_{cm}^2$ = The variance due to differences in the collaborator differences due to method changes, etc.

These components "add," e.g., the variance of repeated measurements by a group of collaborators measuring a value of VC by a method is $\sigma_e^2 + \sigma_c^2$, etc.

In practice, the number of levels actually analyzed was only four because: (a) one level was a "control" level - zero VC and 18.4 ppm acetaldehyde--this level did not "fool" nine of the collaborators in any instance, although Collaborator E did report ~ 7.5 ppm by Methods 1 and 2; (b) the level consisting of 6.8 VC + 45.1 ppm acetaldehyde produced unreliable measurements 40% (16/40) of the time. It is felt that this result is more realistic than a formal numerical analysis of the values (the other 60% of which were reasonably close to the nominal value).

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* Technically, "$\sigma_m^2$" and "$\sigma_L^2$" are not variances, because the methods and levels are fixed (not randomly selected from a population of methods or levels). For convenience, however, the $\sigma^2$ notation will be used.

One collaborator (K) produced obviously discrepant values* at both of the other interfered levels. Therefore, only nine collaborators were incorporated in the primary analysis of variance. Of course, it should be kept in mind during all overall considerations of the method that one (of 10) collaborators did produce unacceptably large errors.

Finally, in the remaining 4 x 4 x 9 = 144 cells, eight values were "missing." These eight were all produced by two collaborators (Collaborators J and E), and were all confined to the two SF-96 methods. The missing values were replaced by a conventional procedure, i.e., by minimizing residual SS within the VC level they fell in.

The analysis of variance results is shown in Table 3. The response (X) is an individual bias, i.e., X = actual reading - NBS reference value.

The results can be summarized as:

* A single collaborator reads a fixed level of VC with a single method within about $\pm$ 0.5 ppm** ($\pm$ 2 $\sigma_e$).

* A set of collaborators reads a fixed level of VC with a given method within about $\pm$ 1.26 ppm ($\pm$ 2 $\sqrt{\sigma_e^2 + \sigma_c^2}$).

* The method effect is quite small, e.g., the so-called "component at variance" $\pm$ 2 $\sqrt{\sigma_e^2 + \sigma_c^2 + \sigma_m^2}$ = $\pm$ 1.30 ppm.

* A set of collaborators reads the various levels of VC in the experiment to within about $\pm$ 1.31 ppm ($\pm$ 2 $\sqrt{\sigma_e^2 + \sigma_c^2 + \sigma_{CL}^2}$).

Of course, in addition to the dispersion of the measurements the accuracy can also be evaluated with respect to the NBS values.*** Various biases of interest are shown in Table 4. In terms of significance:

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* Collaborator K's results for 13.0 ppm VC + 7.1 ppm methanol + 21.1 ppm isobutane were ~ "50 ppm," and for 7.34 ppm VC + 4.5 ppm methanol + 10.6 ppm isobutane were ~ "30 ppm." Both of these results are, of course, rejectable or outliers (Dixon-Massey R = 0.931, $p < 0.005$ and $r = 0.942$, $p < 0.005$).

** This quantity, however, is never directly observed in the experiment.

*** The various biases across levels could be "integrated" via an analysis of covariance with NBS values, a covariate with respect to collaborator values. With only four levels, however, the "piecewise" approach employed is felt to be adequate.

TABLE 3. AOV OF LABORATORY DATA

| Source | aF | SS | MS | F |
|---|---|---|---|---|
| Collaborator (C) | 8 | 43.98 | 5.50 | 91.21[a] |
| Level (L) | 3 | 2.88 | 0.96 | 2.04 |
| Method (M) | 3 | 3.98 | 1.33 | 3.09[b] |
| CL | 24 | 11.21 | 0.47 | 7.79[a] |
| CM | 24 | 10.15 | 0.43 | 7.13[a] |
| LM | 9 | 1.44 | 0.16 | 2.65[b] |
| e | 64 | 3.86 | 0.0603 | |

$EMS\ (C) = \sigma_e^2 + 16\ \sigma_c^2$

$EMS\ (L) = \sigma_e^2 + 4\ \sigma_{CL}^2 + 36\ \sigma_L^2$

$EMS\ (M) = \sigma_e^2 + 4\ \sigma_{CL}^2$

$EMS\ (CL) = \sigma_e^2 + 4\ \sigma_{CM}^2 + 36\ \sigma_M^2$

$EMS\ (CM) = \sigma_e^2 + 4\ \sigma_{CM}^2$

$EMS\ (LM) = \sigma_e^2 + \sigma_{CLM}^2 + 9\ \sigma_{LM}^2$

$EMS\ (CLM) = \sigma_e^2 + \sigma_{CLM}^2$

$EMS\ (e) = \sigma_e^2$

$\sigma_e^2 = 0.0603$

$\sigma_C^2 = 0.3400$

$\sigma_L^2 = 0.0136$

$\sigma_M^2 = 0.0250$

$\sigma_{CL}^2 = 0.1024$

$\sigma_{CM}^2 = 0.0924$

$\sigma_{LM}^2 = 0.0111$

[a] Significant at p = 0.01.

[b] Significant at p = 0.05.

TABLE 4. BIASES IN THE LABORATORY TEST

| Source (ppm) | Avg. bias (ppm) | Bias (%) |
|---|---|---|
| L1 (2.26 VC) | -0.012 | -0.53 |
| L2 (8.57 VC) | -0.219 | -2.56 |
| L3 (13.0 VC + 7.1 methanol + 21.1 isobutane) | -0.386 | -2.97 |
| L4 (7.34 VC + 4.5 methanol + 10.6 isobutane) | -0.083 | -1.13 |
| M1 Chromosorb 102 height | -0.339 | -4.35 |
| M2 Chromosorb 102 area | -0.344 | -4.42 |
| M3 Chromosorb 102 and SF-96 height | +0.014 | +0.18 |
| M4 Chromosorb 102 and SF-96 area | -0.036 | -0.46 |
| Coll. D | +0.200 | +2.57 |
| Coll. H | +0.263 | +3.37 |
| Coll. J | -0.044 | -0.56 |
| Coll. C | +0.500 | +6.42 |
| Coll. G | -0.019 | -0.24 |
| Coll. A | -0.600 | -7.70 |
| Coll. B | -1.325 | -17.01 |
| Coll. F | -0.725 | -9.31 |
| Coll. E | +0.163 | +2.09 |
| All data | -0.176 | -2.26 |

* The bias at all levels was negative (-0.18 ppm overall average), but L1 and L4 were the closest to true, while L2 was significantly more negative, and L3 significantly the most negative. Since L1 and L2 are the pure levels, it is not clear that the interferences cause an increase in bias.

* The two Chromosorb methods (M1 and M2) are significantly more biased than the two Chromosorb + SF-96 methods (-0.34 ppm versus -0.01 ppm). In fact, Methods 3 and 4 are not biased at all. There is no discernible difference between height and area determinations (in either case).

## SECTION 8

## FIELD COLLABORATIVE TEST

The final part of this program was to conduct a test of Method 106 on an actual vinyl chloride source.

A field test was arranged for February 14 through 16 at the Deer Park plant of Diamond Shamrock. Three teams participated in the test. Diamond Shamrock and MRI were teams, and the third team was selected by MRI from the collaborators on the basis of cost.

The sampling was done at ground level from the outlet of a carbon adsorption system. The manifold was connected around a control valve so that a positive flow could be maintained through the manifold. A diagram of the sampling system is shown in Figure 1. Since the line was at a moderate positive pressure, the pumps were not used during sampling. A needle valve was inserted to control the flow into the bags with flow rates still measured by the air leaving the bag enclosure. The expected vinyl chloride concentration was slightly under 1 ppm.

A copy of the letter sent to the collaborators requesting bids for the test is shown in Appendix D. The field test design is given in Tables 5 and 6. The three teams analyzed each others' standards to determine the variability of the different manufacturers' standards. Each team also analyzed some of the other teams' samples to measure precision.

MRI also sampled using carbon adsorption tubes. The adsorption tube procedure followed a modified form of the EPA ambient vinyl chloride method as given in Appendix E. This procedure was compared with the Method 106 results. The method was modified to simplify the calibration procedure and improve the reliability of the method by making the calibration and analysis procedures similar.

The third collaborator selected was Envirotest Laboratories. The personnel who participated in the test were:

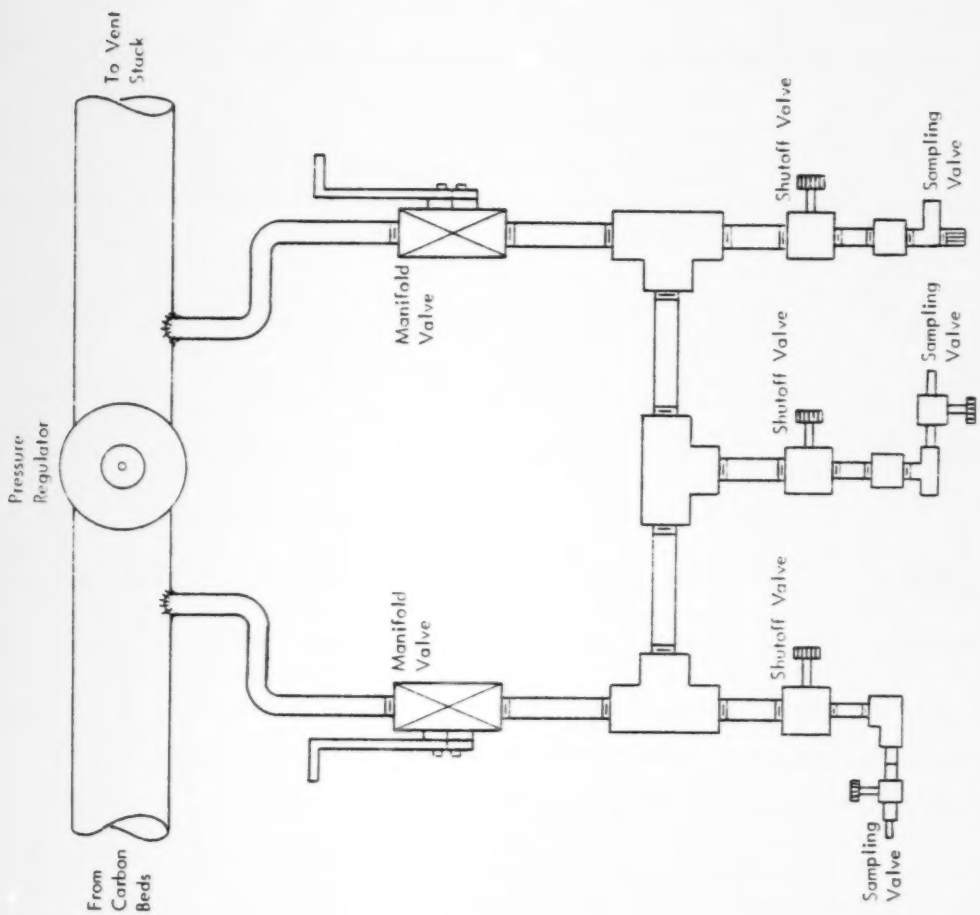


Figure 1. Field test sampling manifold.

TABLE 5. SAMPLING TIME FOR SAMPLE IDENTIFICATION

| | Day 1 | | | | Day 2 | | | |
|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | I | II | III | IV |
| Collaborator A | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $A_6$ | $A_7$ | $A_8$ |
| Collaborator B | $B_1$ | $B_2$ | $B_3$ | $B_4$ | $B_5$ | $B_6$ | $B_7$ | $B_8$ |
| Collaborator C | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ |

TABLE 6. ANALYSIS SEQUENCES

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Day 1 | | | | | | | | | |
| Collaborator A | $S_A$[a/] | $A_1$ | $C_1$ | $A_2$ | $B_2$ | $A_3$ | $C_3$ | $A_4$ | $B_4$ | $S_A$ |
| Collaborator B | $S_B$ | $B_1$ | $A_1$ | $B_2$ | $C_2$ | $B_3$ | $A_3$ | $B_4$ | $C_4$ | $S_B$ |
| Collaborator C | $S_C$ | $C_1$ | $B_1$ | $C_2$ | $A_2$ | $C_3$ | $B_3$ | $C_4$ | $A_4$ | $S_C$ |
| Day 2 | | | | | | | | | |
| Collaborator A | $S_C$ | $A_5$ | $B_5$ | $A_6$ | $B_6$ | $A_7$ | $C_7$ | $A_8$ | $B_8$ | $S_C$ |
| Collaborator B | $S_A$ | $B_5$ | $C_5$ | $B_6$ | $C_6$ | $B_7$ | $A_7$ | $B_8$ | $C_8$ | $S_A$ |
| Collaborator C | $S_B$ | $C_5$ | $A_5$ | $C_6$ | $A_6$ | $C_7$ | $B_7$ | $C_8$ | $A_8$ | $S_B$ |

a/ $S_A$ = Standard gas set belonging to A.

All standards are analyzed by all collaborators twice.
All samples are analyzed by two collaborators.
Each collaborator analyzes all of his samples and one-half of every other collaborators'.

* Envirotest Laboratories
  Mr. Robert Menichelli - analyst
  Dr. Gene Dennison - sampler

* Diamond Shamrock
  Dr. Joseph Banzer - analyst
  Mr. Don Myers - sampler

* Midwest Research Institute
  Dr. George Scheil - analyst
  Mr. John LaShelle - sampler

The field test of Method 106 was completed February 14 through 16, 1978, at the Deer Park plant of Diamond Shamrock. On February 14 equipment was set up and checked by the three teams.

The results of the test are summarized in Tables 7 and 8. On the morning of February 15 a fresh carbon bed was put on line and sampling started for run No. 1 at 0940. Run No. 2 sampled the same carbon bed. The second carbon bed was started prior to run No. 3. Run No. 4 was also made on the second bed. The first three runs proceeded normally with each team analyzing their own bag and one other team's bag during each run. Run No. 4 showed very high vinyl chloride levels caused by intermittent bursts of steam entering the bed which desorbed vinyl chloride. The three bag samples show wide variations in concentration. The variations were probably due to the fact that (according to the plant on-stream analyzer) one of the two steam brusts occurred at the start of sampling when flow rates into the bags were unstable.

During the first test day each collaborator analyzed the other team's standards. Due to the size of one collaborator's standard cylinders it was not feasible to carry them from place to place. Instead, aluminized Mylar bags were filled from each cylinder and analyzed by each collaborator. Thus, one collaborator has different values for peak height and area for their own standards instead of the calibrated values.

On February 16 run Nos. 5 and 6 were made on the first bed after overnight bed regeneration. Run No. 7 started on a fresh second bed but was immediately stopped after another burst of steam. The bags were flushed, pumped down, and checked for contamination. Run No. 7 was then restarted with no further difficulty. No further runs were made since delays from the upsets left no additional time in the test schedule without incurring unscheduled costs.

MRI also ran three charcoal tubes using the tentative procedure which oppears in Appendix E. The results of this comparison are given in Table 9.

# TABLE 7. VINYL CHLORIDE FIELD TEST RESULTS[a/]

| Date Time | | | Collaborator A Samples/standards | | | Collaborator B Samples/standards | | | Collaborator C Samples/standards | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Coll. A analysis | Coll. B analysis | Coll. C analysis | Coll. B analysis | Coll. A analysis | Coll. C analysis | Coll. C analysis | Coll. A analysis | Coll. B analysis |
| Feb. 15 0940-1040 | Run 1 | Ht | 2.72 | | 2.79 | 2.12 | 1.97 | | 1.87 | | 2.14 |
| | | Area | 2.47 | | 3.03 | 2.01 | 1.82 | | 2.02 | | 2.05 |
| Feb. 15 1052-1152 | Run 2 | Ht | 1.55 | 1.73 | | 1.65 | | 1.51 | 1.52 | 1.47 | |
| | | Area | 1.46 | 1.64 | | 1.60 | | 1.64 | 1.68 | 1.44 | |
| Feb. 15 1404-1504 | Run 3 | Ht | 1.05 | | 1.20 | 1.04 | 0.84 | | 0.90 | | 1.15 |
| | | Area | 0.97 | | 1.34 | 1.03 | 0.79 | | 1.03 | | 1.09 |
| Feb. 15 1618-1718 | Run 4 | Ht | 63.7 | 82.0 | | 1,037 | | 898 | 1,280 | 1,207 | |
| | | Area | 73.3 | 82.7 | | 998 | | 897 | 1,280 | 1,362 | |
| Feb. 16 0943-1043 | Run 5 | Ht | 4.34 | 4.64 | | 4.82 | | 4.36 | 3.85 | 3.71 | |
| | | Area | 4.42 | 4.46 | | 4.55 | | 4.42 | 3.86 | 3.75 | |
| Feb. 16 1108-1208 | Run 6 | Ht | 1.89 | | 1.92 | 2.23 | 2.31 | | 1.93 | | 1.99 |
| | | Area | 1.76 | | 1.86 | 2.13 | 2.29 | | 1.88 | | 1.89 |
| Feb. 16 1458-1558 | Run 7 | Ht | 8.14 | | 7.02 | 7.20 | 6.87 | | 5.74 | | 6.26 |
| | | Area | 8.02 | | 7.18 | 7.17 | 6.93 | | 5.78 | | 6.17 |
| | Nominal level | | | | | | | | | | |
| Feb. 15 | 5 ppm standard | Ht | 4.52[b/] | 5.28 | 4.43 | 5.2[c/] | [d/] | 4.55 | 4.79[c/] | [d/] | 5.25 |
| | | Area | 4.61[b/] | 5.05 | 4.62 | 5.2[c/] | 5.0 | 4.58 | 4.79[c/] | 4.86 | 5.26 |
| Feb. 15 | 10 ppm standard | Ht | 9.30[b/] | 10.7 | 8.86 | 10.6[c/] | [d/] | 9.54 | 9.07[c/] | [d/] | 10.1 |
| | | Area | 9.42[b/] | 10.2 | 8.56 | 10.6[c/] | 10.3 | 9.51 | 9.07[c/] | 9.82 | 10.1 |
| Feb. 15 | 50 ppm standard | Ht | 46.1[b/] | 51.6 | 39.8 | 49.0[c/] | [d/] | 42.4 | 41.7[c/] | [d/] | 48.3 |
| | | Area | 45.1[b/] | 49.6 | 38.3 | 49.0[c/] | 47.3 | 42.4 | 41.7[c/] | 48.4 | 47.2 |

a/ All results are reported as parts per million of vinyl chloride.

b/ Manufacturer's measured value.

c/ Manufacturer's certified value.

d/ Collaborator A had instrument problems and height analysis was not obtainable.

## TABLE 8. VINYL CHLORIDE FIELD TEST RESULTS[a/]

| Date Time | | | Collaborator A Samples/standards | | | Collaborator B Samples/standards | | | Collaborator C Samples/standards | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Coll. A analysis | Coll. B analysis | Coll. C analysis | Coll. B analysis | Coll. A analysis | Coll. C analysis | Coll. C analysis | Coll. A analysis | Coll. B analysis |
| Feb. 15 0940-1040 | Run 1 | Ht | 7.04 | | 7.23 | 5.49 | 5.10 | | 4.84 | | 5.54 |
| | | Area | 6.40 | | 7.85 | 5.21 | 4.71 | | 5.23 | | 5.31 |
| Feb. 15 1052-1152 | Run 2 | Ht | 4.01 | 4.48 | | 4.27 | | 3.91 | 3.94 | 3.81 | |
| | | Area | 3.78 | 4.25 | | 4.14 | | 4.25 | 4.35 | 3.73 | |
| Feb. 15 1404-1504 | Run 3 | Ht | 2.72 | | 3.11 | 2.69 | 2.18 | | 2.33 | | 2.98 |
| | | Area | 2.51 | | 3.47 | 2.67 | 2.05 | | 2.67 | | 2.82 |
| Feb. 15 1618-1718 | Run 4 | Ht | 165 | 212 | | 2686 | | 2326 | 3315 | 3126 | |
| | | Area | 190 | 214 | | 2585 | | 2323 | 3315 | 3528 | |
| Feb. 16 0943-1043 | Run 5 | Ht | 11.2 | 12.0 | | 12.5 | | 11.3 | 9.97 | 9.61 | |
| | | Area | 11.4 | 11.6 | | 11.8 | | 11.4 | 10.0 | 9.71 | |
| Feb. 16 1108-1208 | Run 6 | Ht | 4.90 | | 4.97 | 5.78 | 5.98 | | 5.00 | | 5.15 |
| | | Area | 4.56 | | 4.82 | 5.52 | 5.93 | | 4.87 | | 4.90 |
| Feb. 16 1458-1558 | Run 7 | Ht | 21.1 | | 18.2 | 18.6 | 17.8 | | 14.9 | | 16.2 |
| | | Area | 20.8 | | 18.6 | 18.6 | 17.9 | | 15.0 | | 16.0 |
| | Nominal level | | | | | | | | | | |
| Feb. 15 | 12 mg/m$^3$ standard | Ht | 11.7[b/] | 13.7 | 11.5 | 13.5[c/] | [d/] | 11.8 | 12.4[c/] | [d/] | 13.6 |
| | | Area | 11.9[b/] | 13.1 | 12.0 | 13.5[c/] | 13.0 | 11.9 | 12.4[c/] | 12.6 | 13.6 |
| Feb. 15 | 25 mg/m$^3$ standard | Ht | 24.1[b/] | 27.7 | 22.9 | 27.5[c/] | [d/] | 24.7 | 23.5[c/] | [d/] | 26.2 |
| | | Area | 24.4[b/] | 26.4 | 22.2 | 27.5[c/] | 26.7 | 24.6 | 23.5[c/] | 25.4 | 26.2 |
| Feb. 15 | 120 mg/m$^3$ standard | Ht | 119[b/] | 134 | 103 | 127[c/] | [d/] | 110 | 108[c/] | [d/] | 125 |
| | | Area | 118[b/] | 128 | 99 | 127[c/] | 123 | 109 | 108[c/] | 125 | 122 |

a/ All results are reported as milligrams per cubic meter of vinyl chloride.

b/ Manufacturer's measured value.

c/ Manufacturer's certified value.

d/ Collaborator A had instrument problems and height analysis was not obtainable.

TABLE 9. CHARCOAL TUBE SAMPLING RESULTS

| | Charcoal tube analysis[a/] | | | |
|---|---|---|---|---|
| | 2 m SF-96 at 75°C | 2 m Carbowax 1500 on Carbopak at 75°C | Analysis of bag used for charcoal sampling | |
| Run 3 | 0.75 ppm ($1.94\ mg/m^3$) | 0.68 ppm ($1.76\ mg/m^3$) | 0.90 ppm peak ht. ($2.33\ mg/m^3$) | 1.03 ppm peak area ($2.67\ mg/m^3$) |
| Run 6 | 1.75 ppm ($4.53\ mg/m^3$) | 1.55 ppm ($4.01\ mg/m^3$) | 1.93 ppm peak ht. ($5.00\ mg/m^3$) | 1.88 ppm peak area ($4.87\ mg/m^3$) |
| Run 7 | 4.85 ppm ($12.6\ mg/m^3$) | 4.88 ppm ($12.6\ mg/m^3$) | 5.74 ppm peak ht. ($14.9\ mg/m^3$) | 5.78 ppm peak area ($15.0\ mg/m^3$) |

a/ Charcoal tube results were by peak height only.

Each charcoal tube sampled from one of the MRI integrated bag samples after the Method 106 analyses were completed. The original intent of this sampling was to use the same Chromosorb 102 column for the charcoal method analysis. The characteristic doublet impurity peak from carbon disulfide completely obscures the vinyl chloride peak on Chromosorb 102. The first 0.2% Carbowax 1500 on Carbopak column prepared was unusable due to crushing of the fragile Carbopak. An attempt to use a Carbowax 400 column (which has McReynolds constants similar to Carbowax 1500) failed when no vinyl chloride peak could be identified. Finally, the SF-96 secondary column used in Method 106 did achieve a separation of vinyl chloride from the carbon disulfide doublet. However, this nonpolar column results in such a short retention time for vinyl chloride that peak area was unmeasurable and peak height was unstable with 20 to 30% variation in successive injections. The values reported are the averages for duplicate injections, using peak height. The agreement is still quite acceptable between Method 106 and the charcoal tube procedure using the SF-96 column. The carbon disulfide extracts were saved and the results obtained on a new Carbowax 1500/Carbopak column are also given in Table 9. The Carbowax column gave more consistent results although the vinyl chloride retention time is still short.

## SECTION 9

## FIELD TEST STATISTICAL RESULTS

### STANDARDS DATA

In this data set three standards (5, 10, and 50 ppm) were read by three collaborators in the following way: three physical samples (one per collaborator) were taken, and each bag was read by two collaborators. This plan was executed in duplicate according to two methods (M1 = height, M2 = area).

Structurally each method consists of three (one per level) balanced incomplete block (BIB) analysis of variance models.

In practice, one-third of the height measurements were missing, so the formal AOV was performed only for the area method. The height method was separately compared via regression analysis for the 15 cases in which a height value existed.

Finally, casual inspection of the results shows that the magnitude of the components of variance will vary according to the level. For this reason results are quoted separately per level (see Table 10). These results are precisions only, i.e., no bias is included.

Results are:

1. A single collaborator reading a given standard will read within about $\pm$ 0.32 ppm (at VC = 5 ppm), $\pm$ 0.47 ppm (at VC = 10 ppm, and $\pm$ 6.0 ppm (at VC = 50 ppm).

2. A set of collaborators will read a given standard within about $\pm$ 0.59 ppm (at L1), $\pm$ 1.50 ppm (at L2), and $\pm$ 10.2 ppm (at L3).

3. A set of collaborators will read a set of standards within about $\pm$ 0.80 ppm (at L1), $\pm$ 1.92 ppm (L2), and $\pm$ 12.9 ppm (at L3).

4. Roughly speaking, the standard-standard variation is about the same size as the collaborator-collaborator variation.

TABLE 10. RESULTS OF STANDARDS DATA ANALYSIS

A. Analyses of Variance (area method)

Level 1 (5 ppm)

| Source | df | SS | MS | EMS |
|---|---|---|---|---|
| Collaborator (adj) | 2 | 0.2353 | 0.1177 | $\sigma_e^2 + 3/2\ \sigma_C^2$ |
| Sample (s) | 2 | 0.5785 | 0.2916 | $\sigma_e^2 + \sigma_C^2 + 2\ \sigma_S^2$ |
| Error (e) | 1 | 0.0253 | 0.0253 | $\sigma_e^2$ |
| Level 2 (10 ppm) | | | | |
| Collaborator (adj) | 2 | 1.6419 | 0.8210 | $\sigma_e^2 + 3/2\ \sigma_C^2$ |
| Sample (s) | 2 | 2.5375 | 1.2688 | $\sigma_e^2 + \sigma_C^2 + 2\ \sigma_S^2$ |
| Error (e) | 1 | 0.0541 | 0.0541 | $\sigma_e^2$ |
| Level 3 (50 ppm) | | | | |
| Collaborator (adj) | 2 | 68.44 | 34.22 | $\sigma_e^2 + 3/2\ \sigma_C^2$ |
| Sample (s) | 2 | 114.64 | 57.32 | $\sigma_e^2 + \sigma_C^2 + 2\ \sigma_S^2$ |
| Error (e) | 1 | 9.13 | 9.13 | $\sigma_e^2$ |

B. Components of Variance

L1: $\sigma_e^2 = 0.0253$
$\sigma_C^2 = 0.0616$
$\sigma_S^2 = 0.0743$

L2: $\sigma_e^2 = 0.0541$
$\sigma_C^2 = 0.5113$
$\sigma_S^2 = 0.3517$

L3: $\sigma_e^2 = 9.13$
$\sigma_C^2 = 16.73$
$\sigma_S^2 = 15.73$

5. The 5 and 10 ppm results are more or less compatible with the laboratory data; the uncertainties associated with 50 ppm VC are considerably larger (even relatively). It was concluded that the 5, 10, and 50 ppm levels were nominal only, so that quantitative biases were not evaluated.

The comparison of height versus area methods was undertaken via regression analysis of the 15 pairs of such measurements. Results were

$$Ht = -0.15 + 1.03 \text{ (Area)}, \quad r = 0.9998, \quad S_e = 2.47.$$

In this equation the slope is not distinguishable from 1, and the intercept is indistinguishable from zero. Also a t-test of the sample differences is insignificant ($t = 0.60$). Therefore it again appears that there is no worthwhile difference between the two methods.

FIELD SAMPLES

This data set is organized on the same basis as the standards data, except that seven runs (instead of three levels) were executed.

However, on run 4 an anomalous steam burst caused preposterous readings on Samples 2 and 3, so the AOV was restricted to runs 1, 2, 3, 5, 6, and 7. In these data, of course, there are no reference values, so variabilities are the only quantities produced from the analysis. Also, run-run variability was considered a nuisance (the block in a balanced incomplete block design) so that quantification of "$\sigma_R^2$" was not performed.

The 12 balanced incomplete blocks were analyzed individually (Table 11), resulting in aggregate estimates of $\sigma_c^2$, $\sigma_s^2$, and $\sigma_e^2$. The six runs varied (evidently) in VC concentration from about 1 to 8 ppm. The components of variance are significantly larger on R7 than on the other five runs.

A regression analysis of results by method ($M1 = 0.03 + 1.00\ M2$, $r = 0.998$, and $S_e = 0.120$) again fails to indicate any significant difference between them. The other components of variance indicate:

1. A single collaborator reads a single sample to within about $\pm$ 0.33 ppm.

2. A set of collaborators read a given sample to within $\pm$ 0.7 ppm.

3. A set of collaborators read a set of samples (taken "simultaneously") to within about $\pm$ 0.91 ppm.

4. Sampling variability contributes about $\pm$ 0.58 ppm to the method's error limits.

TABLE 11. DATA ANALYSIS OF FIELD TEST

| | | (M1)[a/] | (M2)[b/] |
|---|---|---|---|
| Run 1 ($\overline{VC}$ = 2.25) | $\sigma_{e_2}^2$ = | 0.0280 | 0.0267 |
| | $\sigma_{c_2}^2$ = | 0 | 0.0317 |
| | $\sigma_s^2$ = | 0.1641 | 0.1746 |
| Run 2 ($\overline{VC}$ = 1.57) | $\sigma_{e_2}^2$ = | 0.0001 | 0.0001 |
| | $\sigma_{c_2}^2$ = | 0.0091 | 0.0152 |
| | $\sigma_s^2$ = | 0.0008 | 0 |
| Run 3 ($\overline{VC}$ = 1.04) | $\sigma_{e_2}^2$ = | 0.0067 | 0.0060 |
| | $\sigma_{c_2}^2$ = | 0.0141 | 0.0237 |
| | $\sigma_s^2$ = | 0 | 0.0005 |
| Run 5 ($\overline{VC}$ = 4.27) | $\sigma_{e_2}^2$ = | 0.0150 | 0.0067 |
| | $\sigma_{c_2}^2$ = | 0.0385 | 0 |
| | $\sigma_s^2$ = | 0.1683 | 0.1413 |
| Run 6 ($\overline{VC}$ = 2.01) | $\sigma_{e_2}^2$ = | 0.0048 | 0.0121 |
| | $\sigma_{c_2}^2$ = | 0 | 0 |
| | $\sigma_s^2$ = | 0.0364 | 0.0392 |
| Run 7 ($\overline{VC}$ = 6.87) | $\sigma_{e_2}^2$ = | 0.1441 | 0.0794 |
| | $\sigma_{c_2}^2$ = | 0.1282 | 0.0732 |
| | $\sigma_s^2$ = | 0.5080 | 0.6069 |
| All Runs ($\overline{VC}$ = 3.00) | $\sigma_{e_2}^2$ = | 0.0331 | 0.0218 |
| | $\sigma_{c_2}^2$ = | 0.0317 | 0.0240 |
| | $\sigma_s^2$ = | 0.1462 | 0.1604 |
| All data ($\overline{VC}$ = 3.00) | $\sigma_{e_2}^2$ = | 0.0275 | |
| | $\sigma_{c_2}^2$ = | 0.0279 | |
| | $\sigma_s^2$ = | 0.1533 | |

a/ Peak height.

b/ Peak area.

Although qualitatively comparable, it can be seen that the field results are somewhat more precise than the laboratory data ($\pm$ 0.91 ppm versus $\pm$ 1.26 ppm). This is because the three collaborators used in the field test are much more alike than the 10 collaborators used in the first test.

## REFERENCES


1. Federal Register 40:59477, December 24, 1975.

2. Federal Register 41:46564-46573, October 21, 1976.

APPENDIX A

LETTER TO OBTAIN POTENTIAL COLLABORATORS

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600

You are invited to participate in a collaborative test of a modified version of EPA Method 106 - "Determination of Vinyl Chloride From Stationary Sources," a copy of which is enclosed. Midwest Research Institute (MRI) is under contract to the U.S. Environmental Protection Agency to conduct this collaborative test. The test will consist of two parts: a laboratory test of the analysis procedure and a field test of the entire method.

For the laboratory test a minimum of eight collaborators will each receive a set of six samples of vinyl chloride with various interferences present in some of the samples. Each sample will be supplied in a 3-liter capacity (at STP) aerosol-type can. A heated sampling valve must be used. Injection by syringe is not acceptable.

Samples will be introduced into the sample valve loop by inserting the needle on the sample can through a septum mounted in the line going to the valve. Since the sample flow is under positive pressure, no sample pump is used. Each sample will be analyzed in triplicate using two different columns--a 2 m x 3.2 mm OD stainless steel column packed with 60/80 Chromosorb 102 and a composite column consisting of the Chromosorb 102 column followed by a 2 m x 3.2 mm OD stainless steel column packed with 20% SF-96 on 60/80 mesh AW Chromosorb P. Vinyl chloride concentrations on each sample/column combination are to be calculated by both peak area and peak height. The original strip chart recordings must be submitted to MRI with the results.

The sample cans must be returned to MRI after the analyses with sufficient pressure to allow a final check for stability.

Cylinders containing approximately 5, 10, and 50 ppm vinyl chloride in nitrogen are to be used as standards and will not be supplied by MRI. Each cylinder must be certified by the manufacturer by comparison against (a) a gravimetrically calibrated vinyl chloride permeation tube, (b) a vinyl chloride gas mixture analyzed by the National Bureau of Standards, or (c) standard gas mixtures prepared in accordance with Section 7.1 of Method 106.

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 641
Telephone (816) 753-76

If you are interested in participating in the laboratory test of the method, you are asked to submit a firm, fixed price bid for the collaborative test. The collaborators will be selected on the basis of the analyst's experience in the analysis of vinyl chloride, the analyst's experience in gas chromatography, the ability to supply the necessary equipment for the test, and cost. The experience of the person who will perform the analysis and the model numbers of the gas chromtograph and sample valve that will be used should be submitted with your bid. The person performing the analysis is designated as Key Personnel. If this person does not perform the analyses the contract may be declared void. Bids must be received by April 15, 1977. The samples will be sent on or about June 15th and results must be submitted to MRI within 1 month.

The field test of the method will consist of a small group of collaborators obtaining samples and analyzing the samples at a vinyl chloride plant. Collaborators will obtain duplicate samples with a minimum of three sets of samples per day for 2 days of testing. For this test each collaborator must be able to supply the necessary Tedlar bags and enclosures. All samples must be analyzed within 72 hr. This requires either a gas chromatograph which can be taken to the test area or provision for rapid shipment and analysis after each test. A crew of two is anticipated for each collaborator. The site for the field test has not been selected. You are asked to indicate your interest in participating in the field test. If interested, please state the model number of the gas chromatograph which would be used and the number of rigid leakproof containers with 100 liter Tedlar bags that you could supply for the test. MRI is not at this time soliciting bids for the field test.

If you have any questions in regard to the test, please call George Scheil or Paul Constant at (816) 753-7600.

Sincerely,

MIDWEST RESEARCH INSTITUTE

George W. Scheil
Associate Chemist

Enclosures

GWS:sw

APPENDIX B

FINAL INSTRUCTIONS TO COLLABORATORS

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600

July 28, 1977

The EPA sponsored collaborative test of Method 106 - "Determination of Vinyl Chloride from Stationary Sources," has now started. Your laboratory is one of the 10 collaborators selected for the laboratory test of the procedure. This letter is to inform you of the revised test schedule and other changes in the test.

Each collaborator should receive six cylinders of vinyl chloride in nitrogen during the week of September 12, 1977. These cylinders may or may not contain vinyl chloride and interferences. The sample cylinders are moderate pressure Freon-type canisters with a volume of about 8 $ft^3$ (at STP). An adapter to connect the cylinders to 1/4 in. Swagelok fittings will be supplied. If you prefer a different adapter, please contact MRI. The samples are introduced into the sample valve loop via Teflon tubing by partially opening the cylinder valve. A stainless steel valve or capillary restrictor may be needed to limit flow into the sample loop. A sample pump is not needed.

Each sample will be analyzed in triplicate using two different columns--a 2 m x 3.2 mm OD stainless steel column packed with 60/80 Chromosorb 102 and a composite column consisting of the Chromosorb 102 column followed by a 2 m x 3.2 mm OD stainless steel column packed with 20% SF-96 on 60/80 mesh AW Chromosorb P. Vinyl chloride concentrations on each sample/column combination are to be calculated by both peak area and peak height. The original strip chart recordings must be submitted to MRI with the results. The chart recordings and calculated results for all six samples must be mailed to MRI by October 15, 1977.

The sample cylinders should be saved with sufficient pressure for additional measurements until MRI has reviewed your results. After your results have been examined at MRI you will be notified if the samples need to be returned to MRI to resolve any questions. If your results are satisfactory you may keep the sample cylinders.

Cylinders containing approximately 5, 10, and 50 ppm vinyl chloride in nitrogen are to be used as standards and will not be supplied by MRI. Each cylinder must be certified by the manufacturer by comparison against: (a) a gravimetrically calibrated vinyl chloride permeation tube; (b) a vinyl chloride gas mixture analyzed by the National Bureau of Standards; or (c) standard gas mixtures prepared in accordance with Section 7.1 of Method 106.

These requirements have been published in the Federal Register and a copy is attached together with a copy of the Method 106 procedure. The gas supplied should provide a certificate stating compliance with the Federal Register requirements. Please send MRI copies of the certificates with your data.

A check of several gas suppliers indicates that Matheson and Air Products do not supply vinyl chloride standards. Airco in Riverton, New Jersey, Analabs in North Haven, Connecticut, and Scott Specialty Gases in Plumsteadville, Pennsylvania, state that they can supply standards which conform to the Federal Register requirements.

You will receive additional information regarding the field test at a later date. If you have any questions in regard to the test, please call Dr. George Scheil or Mr. Fred Bergman at (816) 753-7600.

Sincerely,

George W. Scheil
Associate Chemist

GWS:clk

Enclosure

APPENDIX C

METHOD 106 - DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES WITH AMENDMENTS

## Method 106—Determination of Vinyl Chloride from Stationary Sources

### Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability.

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethylene) is subjected to chromatographic analysis, using a flame ionization detector.

1.2 The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

2. Range and Sensitivity.

The lower limit of detection will vary according to the chromatograph used. Values reported include $1 \times 10^{-7}$ mg and $4 \times 10^{-7}$ mg.

3. Interferences.

Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromosorb 102 column. See sections 4.3.2 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then chromatograph parameters can be further altered with prior approval of the Administrator. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

4. Apparatus.

4.1 Sampling (Figure 1).

4.1.1 Probe—Stainless steel, Pyrex glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line—Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 1.

4.1.4 Tedlar bags, 100 liter capacity—To contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collection.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle valve—To adjust sample flow rate.

4.1.7 Pump—Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube—To prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flow meter—For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 Connecting tubing—Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 1).

4.1.11 Pitot tube—Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.2 Sample recovery.

4.2.1 Tubing—Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas chromatograph—With flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 Chromatographic column—Stainless steel, 2.0 × 3.2 mm, containing 80/100 mesh Chromosorb 102. A secondary colum of GE SF-96, 20% on 60/80 mesh AW Chromosorb P, stainless steel, 2.0 m × 3.2 mm, will be required if acetaldehyde is present. If used, the SF-96 column is placed after the Chromosorb 102 column. The combined columns should then be operated at 110°C.

4.3.3 Flow meters (2)—Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators—For required gas cylinders.

4.3.5 Thermometer—Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer—Accurate to 5 mm Hg, to mensure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump—Leak-free. Minimum capacity 100 ml/min.

4.4 Calibration.

4.4.1 Tubing—Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags—Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe—0.5 ml, gas tight.

4.4.4 Syringe—50-µl, gas tight.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to ±1%, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch—Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas—Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas—Zero grade.

5.1.3 Oxygen gas, or Air, as required by the detector—Zero grade.

5.2 Calibration.

5.2.1 Vinyl chloride, 99.9+%—For preparation of standard gas mixtures.

5.2.2 Calibration cylinders (3), optional—One each of 50, 10 and 5 ppm vinyl chloride in nitrogen with certified analysis. Analysis must be traceable to NBS (National Bureau of Standards) or to a gravimetrically calibrated vinyl chloride permeation tube.

5.2.3 Nitrogen gas—Zero grade, for preparation of standard gas mixtures.

6. Procedure.

6.1 Sampling. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Sample bags must be kept out of direct sunlight. When at all possible, analysis is to be performed within 24 hours of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0–100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 100° C, the detector temperature to 150° C, and the sample loop temperature to 70° C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed

[1] Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.



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and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, $A_m$, by use of $H_m$, and a disc integrator or a planimeter. Measure the peak height, $H_m$. Record $A_m$ and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.

Compare the ratio of $H_m$ to $A_m$ for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10%, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2).

6.5 Measure the ambient temperature and barometric pressure near the bag. (Assume the relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine the record and water vapor content of the bag.

7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 µl of 99.9+% vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. This gives a concentration of 50 ppm of vinyl chloride. In a like manner use the other syringe to prepare dilutions having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases.

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3, above. Set attenuator to X 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time. Record.

7.3 Preparation of chromatograph calibration curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 7.1) using conditions identical with those listed in Section 6.3 above. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record $C_s$, the concentrations of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate $A_s$, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5%, then plot those points vs $C_s$. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

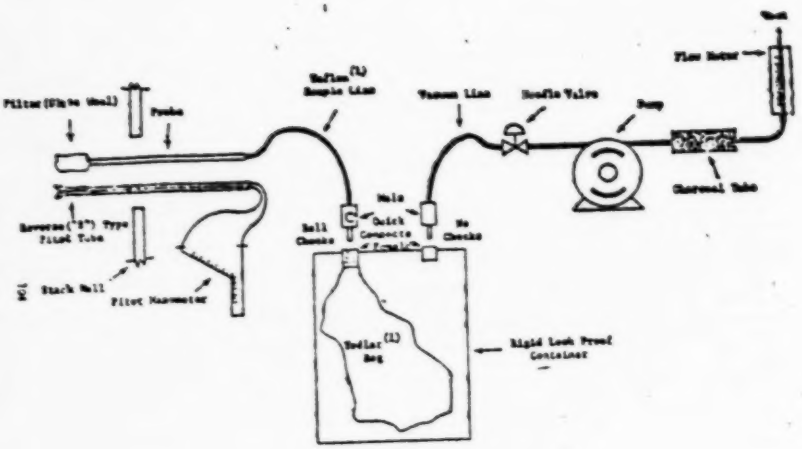


Figure 106-1. Integrated bag sampling train.

(1) Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 5-10 cm $H_2O$ (2-4 in $H_2O$). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also check the rigid container for leaks in this manner.

(NOTE: An alternative leak check method is to pressurize the bag to 5-10 cm $H_2O$ or 2-4 in. $H_2O$ and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_s = A_m A_f$$

Equation 106-1

where:
$A_s$ = The sample peak area.
$A_m$ = The measured peak area.
$A_f$ = The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3, above, select the value of $C_s$ that corresponds to $A_s$, the sample peak area. Calculate $C_b$ as follows:

$$C_b = \frac{C_s P_r T_s}{P_s T_r (1 - B_{ws})}$$

Equation 106-2

Where:
$B_{ws}$ = The water vapor content of the bag sample, as analyzed.
$C_b$ = The concentration of vinyl chloride in the bag sample in ppm.
$C_s$ = The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.
$P_r$ = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.
$T_s$ = The sample loop temperature on the absolute scale at the time of analysis, °K.
$P_s$ = The laboratory pressure at time of analysis, mm Hg.
$T_r$ = The reference temperature, the sample loop temperature recorded during calibration, °K.

9. References.

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia, June 24, 1974.

2. "Evaluation of A Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report oN. 75-VCL-1.

3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract No. 68-02-1098, Task Order No. 7.



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9. Section 1.1 of Test Method 106 is corrected as follows:

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to chromatographic analysis, using a flame ionization detector.

10. Section 3 of Test Method 106 is corrected as follows:

3. *Interferences.* Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromasorb 102 column. See sections 4.3.2 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then chromatograph parameters can be further altered with prior approval of the Administrator. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

11. Section 4.1 of Test Method 106 is corrected as follows:

4.1 *Sampling* (Figure 106-1).

12. Section 4.1.3 of Test Method 106 is corrected as follows:

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 106-1.

13. Section 4.1.10 of Test Method 106 is corrected as follows:

4.1.10 *Connecting tubing.* Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 106-1).

14. Section 4.3.2 of Test Method 106 is amended as follows:

4.3.2 *Chromatographic column.* Stainless steel, 2 m×3.2 mm, containing 80/100 mesh Chromasorb 102. A secondary column of GE SP-96, 20 percent on 60/80 mesh AW Chromasorb P, stainless steel, 2 m×3.2 mm or Porapak T, 80/100 mesh, stainless steel, 1 m×3.2 mm is required if acetaldehyde is present. If used, a secondary column is placed after the Chromasorb 102 column. The combined columns should then be operated at 120° C.

15. Section 5.2 of Test Method 106 is revised as follows:

5.2 *Calibration.* Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 *Vinyl chloride, 99.9+ percent.* Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 *Nitrogen gas.* Zero grade, for preparation of standard gas mixtures.

5.2.3 *Cylinder standards* (3). Gas mixture standards (50, 10, and 5 ppm vinyl chloride in nitrogen cylinders) for which the gas composition has been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in section 7.3.

5.2.3.1 *Cylinder standards certification.* The concentration of vinyl chloride in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 50 and 100 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique used.

5.2.3.2 *Establishment and verification of calibration standards.* The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a calibrated vinyl chloride permeation tube, (2) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in section 7.1 and using 99.9+ percent vinyle chloride, or (3) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.

16. Section 6.2 of Test Method 106 is amended as follows:

6.2 *Sample storage.* Sample bags must be kept out of direct sunlight. When at all possible analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection.

17. Section 7.1 of Test Method 106 is amended as follows:

7.1 *Preparation of vinyl chloride standard gas mixtures.* Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250ml of 99.9+ percent vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm. In a like manner use the other syringe to prepare gas mixtures having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time preparation of new gas mixtures is required. (CAUTION—Contamination may be a problem when a bag is reused if the new gas mixture standard contains a lower concentration than the previous gas mixture standard did.)

18. Section 7.3 of Test Method 106 is amended as follows:

7.3 *Preparation of chromatograph calibration curve.* Make a gas chromatographic measurement of each gas mixture standard (described in section 5.2.2 or 7.1) using conditions identical with those listed in sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record $C_c$, the concentration of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate $A_c$, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5 percent, then plot these points v. $C_c$. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.



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RETENTION INDICES FOR POSSIBLE VINYL CHLORIDE INTERFERENCES

TABLE C-1. RETENTION INDICES FOR POSSIBLE VINYL CHLORIDE INTERFERENCES

| | 2 m Chromosorb 102 100°C | 2 m Chromosorb 102 + 1 m Porapak T 120°C | 2 m Chromosorb 102 + 2 m SF-96 120°C | 2 m Chromosorb 102 + new 2 m SF-96 120°C |
|---|---|---|---|---|
| Methane* | 100 | 100 | 100 | 100 |
| Ethylene | 180 | 180 | 175 | - |
| Ethane* | 200 | 200 | 200 | 200 |
| Propane* | 300 | 300 | 300 | 300 |
| Methyl chloride | 320 | 340 | 320 | 325 |
| Methanol | 330 | 395 | 350 | 375 (low levels retained) |
| Acetaldehyde | 355 | 400 | 375 | 400 (low levels retained) |
| Ethylene oxide | 355 | 395 | 375 | - (low levels retained) |
| Vinyl chloride | 360 | 375 | 360 | 360 |
| Isobutane | 380 | 380 | 380 | 380 |
| Isobutylene | 395 | 395 | 385 | 390 |
| 1-Butene | 395 | 395 | 395 | - |
| n-Butane* | 400 | 400 | 400 | 400 |
| 1,3-Butadiene | 400 | 410 | 395 | 395 |
| trans-2-Butene | 400 | 410 | 400 | - |
| Ethanol | 415 | 475 | 435 | - |
| Ethyl chloride | 415 | 430 | 415 | 410 |
| cis-2-Butene | 415 | 415 | 410 | - |
| 1,1-Dichloroethylene | 480† | 490† | 480† | - |
| trans-1,2-Dichloroethylene | 510† | 495† | 505† | - |

* Reference compounds for indices.

† Column at 150°C.

APPENDIX D

LETTER TO COLLABORATORS

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600

December 1, 1977

The results of the laboratory part of the collaborative test of EPA Method 106 are now complete. The preliminary analysis of the data indicates that no serious errors occurred. A few chromatograms were misinterpreted and two collaborators did not detect any acetaldehyde with the chromosorb 102 column. The contents of the samples are given in the the table attached. Vinyl chloride and isobutane have proved to be stable. The acetaldehyde concentration is decaying gradually in most samples and methanol has either disappeared or is eluting with isobutane. The chromosorb 102 column should have resolved all samples except 1814, but acetaldehyde is retained on the SF-96 column. The separation of isobutane is usually reduced on SF-96. Analyses conducted by NBS was only for vinyl chloride.

| Sample No. | Components ($N_2$ Balance) | Vinyl Chloride Found by NBS (ppm) |
|---|---|---|
| 1814 | 6.8 ppm vinyl chloride<br>45.1 ppm acetaldehyde | 6.75 |
| 4036 | 13.0 ppm vinyl chloride<br>7.1 ppm methanol<br>21.1 ppm isobutane | 13.0 |
| 4786 | 8.73 ppm vinyl chloride | 8.57 |
| 6800 | 7.04 ppm vinyl chloride<br>4.5 ppm methanol<br>10.6 ppm isobutane | 7.34 |
| 10673 | 18.4 ppm acetaldehyde | 0.05 |
| 60106 | 2.24 ppm vinyl chloride | 2.26 |

The field part of the collaborative test of EPA Method 106 under MRI's prime EPA Contract No. 68-02-2737 is scheduled for February 14-16, 1978. The test will be conducted at the Diamond Shamrock facilities in Deer Park, Texas. The participants in the laboratory test are requested to submit fixed-price bids if they are interested in participating in the field test. A total of three groups will conduct simultaneous sampling from a manifold. Each collaborator must have two personnel on the site, a sampler and a gas chromatograph operator. The person who preformed the original laboratory analyses must be the GC operator and shall be designated as key personnel for this test.

Each team must provide the following equipment for the test:

1. A gas chromatograph (FID) with gas sampling valve and recorder.
2. Three calibration gas cylinders (5, 10, and 50 ppm vinyl chloride).
3. A minimum of 2 tested 100 liter bags and enclosures as required by Method 106. Tedler or aluminized Mylar bags are acceptable.
4. Rotameter, pump, and other necessary items to obtain samples from the manifold and perform leak tests.

An area (indoors) will be provided for the chromatographs. Air, hydrogen, and carrier gas will be provided to all teams as well as suitable 110 V AC power. The samples will probably contain low levels of vinyl chloride. The instrument used must have sufficient sensitivity to accurately measure vinyl chloride as low as 0.5 ppm.

Since sampling will be done from a common (ground level) manifold, no pitot or oxygen measuring equipment is needed. Sampling will be done at a constant rate of about 0.5 pm for 1 hr periods. The manifold will probably be under slight positive pressure so that the pump can be removed during sampling, although it must be available for emptying bags and making leak checks. The sampling will be done in a restricted access area where explosion-proof pumps are required. If an AC pump is used it must be inside an explosion-proof or inert purged housing. Battery driven approved personnel sampling-type pumps are also acceptable.

The tentative work schedule is:

February 14 - Set-up and test equipment.

February 15 - Sampling - each team will collect 4 samples. Analysis - each team will analyze their own vinyl chloride standards and one of the other teams' standards. Each team will also analyze their own 4 samples and 4 samples obtained by other teams.

February 16 - Same as February 15; pack equipment and clear the site.

Each test day should be completed within 8-10 hr. All samples and standards will be analyzed in triplicate in the same manner as used in the laboratory collaborative test, except that only one column will be used. Each team must bring both the Chromosorb 102 and SF-96 columns to the test and the column(s) to be used will be selected on the set-up day. All samples will be measured by peak height and area, and the original recorder charts must be sent to MRI.

The participants will be chosen on the basis of ability to meet the necessary requirements, performance on the laboratory test, and cost. Firm, fixed-price bids must be submitted to MRI by January 4, 1978 to be considered. Technical questions should be referred to Dr. George Scheil. Contractual questions should be referred to Ms. Sequin Lukon. The MRI phone number is (816) 753-7600.

Sincerely,

MIDWEST RESEARCH INSTITUTE

George Scheil
Associate Chemist

GS:sw

APPENDIX E

# TENTATIVE PROCEDURE FOR SAMPLING AND ANALYSIS OF VINYL CHLORIDE USING CHARCOAL ADSORPTION TUBES

December 1977

# TENTATIVE METHOD FOR THE DETERMINATION OF VINYL CHLORIDE

1. Principle and Applicability.

1.1 Vinyl chloride (chloroethene) is absorbed from air onto charcoal adsorbers, which are subsequently extracted with carbon disulfide. The resulting solutions are then measured chromatographically, using a flame ionozation detector.

1.2 The method is applicable to the measurement of vinyl chloride in ambient air using a 24-hour sampling period.*

2. Range and Sensitivity. The limit of detection is approximately 0.003 $mg/m^3$ (1 ppb). The maximum of the range is 20 $mg/m^3$ (8 ppm); it may be increased by extending the calibration range or by diluting the sample.

3. Interferences. At the present time, there are no known common pollutants in the ambient atmosphere in sufficient concentrations to interfere with the measurement of vinyl chloride. However, certain volatile hydrocarbons and Freons have elution characteristics similar to vinyl chloride.

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* Warning: Vinyl chloride is a suspected carcinogen. Care must be exercised to protect operators from breathing vinyl chloride fumes. Carbon disulfide is toxic and its vapors form explosive mixtures with air. Work with this material in a well ventillated fume hood.

Among the latter is Freon 12 (dichlorodifluoromethane). Under certain conditions, a peak is associated with the injection and subsequent withdrawal of the microsyringe into and from the G.C. septum. These peaks can also give interferences with the vinyl chloride peak.

4. Precision and Accuracy. Replicate gas chromatographic analyses of standard gas mixtures and sample aliquots should not deviate by more than 3 per cent relative standard deviation. When the entire analysis is repeated, preliminary studies indicate that relative standard deviations of 6 per cent are attainable. No information is presently available on accuracy.

5. Apparatus.

5.1 Sampling - Air Monitoring materials.

5.1.1 Pump - Capable of maintaining an air pressure differential greater than 0.5 atmospheres at the desired flow rate.

5.1.2 Critical Orifice - Twenty-seven gauge 3/8" hypodermic needle. To control flow rate at approximately 200 ml/min.

5.1.3 Tubing - 18 cm length of 10 mm O.D. borosilicate glass with tapered ends, to prepare adsorption tube.

5.1.4 Serum caps - 5 x 9 mm and 7 x 11 mm sizes.

5.1.5 Vibrator - To achieve close packing of the adsorption tube.

5.1.6 Air flow meter - Rotometer type; 1 - 260 ml/min range. To calibrate critical orifice.

5.1.7 Furnace, muffle - To operate at 400°C.

5.2 Sample recovery.

5.2.1 Graduated cylinder - Glass stoppered; capacity, 25 ml (TC).

5.2.2 Pipette, dropping - 2 ml.

5.2.3 Serum bottle - Narrow mouth for septum sealing; 2 ml.

5.2.4 Serum cap - With Teflon coating on the side of the septum exposed to the sample 5 x 9 mm size. (Hewlett-Packard #5080-8713[1] has been found to be satisfactory).

5.2.5 Aluminum serum cap seal.

5.2.6 Crimper - For use with aluminum serum cap seals.

5.3 Analysis.

5.3.1 Gas chromatograph - With flame ionization detector and potentiometric strip chart recorder.

5.3.2 Chromatographic column - stainless steel, 2.5 m x 3.2 mm O.D., containing 0.4% Carbowax 1500 on Carbopak A packing. (w/w)

5.3.3 Microsyringe - 0 to 10 microliter range, graduated.

5.3.4 Gas regulator - 4 to 50 psig range.

5.3.5 Needle valve - to control standard gas flow.

5.3.6 Teflon tubing - 10 mm O.D.

5.3.7 Tygon tubing sleeve - 10 mm I.D.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6. Reagents

Unless otherwise indicated, it is intended that all reagents be chromatographic grade or conform to the specifications established by the Committee of Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use best available grade.

6.1 Sampling.

6.1.1 Charcoal - Activated coconut shell charcoal. (Fisher Scientific Company,[1] 6 to 14 mesh is effective.)

6.1.2 Glass wool - borosilicate

6.1.3 Aluminum foil.

6.2 Sample recovery.

6.2.1 Carbon disulfide.

6.3 Analysis.

6.3.1 Nitrogen gas - Zero grade, for chromatographic carrier gas and for preparation of standard gas samples.

6.3.2 Vinyl chloride - 128, 25.6, and 12.8 $mg/m^3$ at 25 C, 1 atm 50 ppm v/v, in zero nitrogen. Analyzed. For calibration.

6.3.3 Combustion Air - Containing less than 1.3 $mg/m^3$ hydrocarbons (2 ppm as methane). To operate flame ionization detector.

7. Procedure.

7.1 Sampling.

7.1.1 Activation of charcoal - Heat charcoal to 400°C for one hour to remove adsorbed gases. Store in a sealed container.

7.1.2 Preparation of adsorption tube - Insert glass wool into tubing (see Section 5.1.3) and tamp into position at one end to a depth of approximately 2.5 cm. Mount tube on vibrator in a verticle position. Add charcoal a little at a time and vibrate after each addition to prevent channelling. Fill tube to a depth of 13 cm with charcoal. Insert glass wool into remainder of tube. Prepare additional adsorption tubes in a similar and uniform manner. Cover ends of tubes with serum caps. Wrap with aluminum foil to protect tubes from light during storage and subsequent use. Insert critical orifice through septum at one end of tube. Retain until calibration, sampling and recalibration procedures have been completed. Sufficient tubes should be prepared from a single lot of charcoal to complete the sample analysis and associated calibration.

7.1.3 Sample collection. Remove serum cap from one end of the adsorption tube and mount it with open end downward. Connect critical orifice to the sampling train. Begin drawing air through the tube. Record time and adsorption tube number. Continue sampling for 1 hr. At end of sampling interval, record time, disconnect adsorption tube from sampling train and protect open end with serum cap. Remove sample to analytical area. Protect tube from light.

7.2 Sample recovery. Fill the graduated cylinder to the 25 ml mark with carbon disulfide, stopper and cool in an ice bath. Remove cap and glass wool from one end of the adsorption tube and, with continued cooling, rapidly add charcoal to the carbon disulfide. Stopper cylinder immediately. (Note: the mixing of charcoal and carbon disulfide is an exothermic process

that causes local boiling of the solution. The mixture must be cooled and the container stoppered to prevent loss of vinyl chloride.) Mix thoroughly. Allow mixture to stand for one half-hour in the ice bath. Mix throughly and draw off 2 ml of the supernatant liquid. Completely fill 2 ml serum bottle, cap and seal.

7.3 Analysis.

7.3.1 Column preconditioning. Prior to its initial use, the chromatographic column is heat treated to remove impurities. To do this, establish a 40-60 ml/min flow of zero nitrogen through the column and raise its temperature from ambient by 2°C/min to 200°C. Maintain these conditions for 48 hours, or until base line drift is eliminated.

7.3.2 Chromatographic analysis. Set the column temperature to 60°C and the sample inlet port temperature to at least 170°C. Operate the flame ionization detector at the temperature specified by the manufacturer. Using zero nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for the satisfactory detector operation. A flow rate of 40 ml/min has been shown to produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base-line drift has ceased. Inject a 2.5 microliter aliquot of the supernatant solution of the sample into the gas chromatograph. Mark the injection point on the chart. (The injection point is defined as the position of the pen on the chart at the time of sample injection.) Record the sample number, the column temperature, carrier gas flow rate, chart speed and the attenuator

setting. From the chart, select the peak having the retention time corresponding to vinyl chloride. (See Section 8.3 below). Measure the peak height, $H_m$, the distance in chart divisions from the average value of the baseline to the maximum of the wave form. Record $H_m$ and the retention time. Purge the column at 160°C for five minutes.

8. Calibration and Standards.

8.1 Calibration of absorption tube flow rates. Connect absorption tube to sampling train as in 7.1.3, above. Connect flowmeter in series. Turn on pump and measure flow rate. Record rate and adsorption tube number. Repeat flow rate calibration procedure after sample collection. Denote flow rate before sampling as $F_1$; denote flow rate after sampling as $F_2$.

8.2 Preparation of vinyl chloride standard mixtures. Connect regulator to the 12.8 $mg/m^3$ standard gas cylinder as shown in Figure 12.2. Put needle valve on regulator outlet. Remove serum caps from a fresh adsorption tube. Connect needle valve to the adsorption tubes with 10 mm Teflon tubing using an end-to-end sleeve joint at the inlet end of the adsorption tube. Connect rotometer to outlet side of the adsorption tube.

Disconnect sleeve on inlet of adsorption tube. Purge sample line briefly, venting gas in a safe area. Reconnect line and set flow rate to 200 ml/min. Sample cylinder gas for 1 hr, maintaining constant flow. Record sampling start and stop times, inital and final flow rates, tube number, and cylinder vinyl chloride concentration. Disconnect adsorption tube and

replace serum caps. Repeat with fresh adsorption tubes using the 25.6 and 128 $mg/m^3$ standards. Recover the standard samples following the procedure described in 7.2.

8.3 Determination of vinyl chloride retention time. Establish chromatographic conditions identical with those in 7.3.2 above. Set attenuator to X 1 position. Inject a 2.5 $\mu$l portion of carbon disulfide into gas inlet port. Mark the injection point on the chart and record the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. Inject 2.5 $\mu$l of the 12.8 $mg/m^3$ standard into gas chromatograph. Mark the injection point on the chart. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart in mm from the injection point to the peak maximum. This distance, divided by the chart speed in mm/min, is defined as the retention time. Record.

8.4 Preparation of chromatograph calibration curve. Make a gas chromatographic measurement of each standard mixture described in Section 8.2 (12.8 through 128 $mg/m^3$), using conditions identical with those listed in Section 7.3.2, above. Record $W_{vc}$, $V_m \times C_{vc} \times Vi/Vs$, the attenuator setting, chart speed, peak height and retention time. Calculate $H_c$, the peak height multiplied by the attenuator setting. Plot $W_{vc}$ vs $H_c$. Repeat until replicate measurements do not deviate by more than 3% relative standard deviation and draw a smooth curve through the points. Check calibration after every fifth analysis using the 12.8 $mg/m^3$ (5 ppm) standard mixture

and either the 25.6 or 128 mg/$m^3$, whichever exceeds the highest unknown analyzed. Recalibrate daily, and whenever remeasurement of a standard gas sample deviates from its calibration value by more than 6%.

9. Calculations.

9.1 Uncorrected volume. The volume of air sample is not corrected to S.T.P., because of the uncertainty associated with 24-hr average temperature and pressure values. Determine the air sample volume taken for analysis.

$$V_m = \frac{F_1 + F_2}{2} \times T \times 10^{-6},$$

where:

$V_m$ = The volume of gas sampled (uncorrected), $m^3$.

$F_1$ = The measured flow rate before sampling, ml/min.

$F_2$ = The measured flow rate after sampling, ml/min.

T = The sampling time, min.

9.2 Determine the sample peak height as follows:

$$H_c = H_m A_m,$$

where:

$H_c$ = The sample peak height, chart divisions.

$H_m$ = The measured peak height, chart divisions.

$A_m$ = The attenuator setting.

9.3 Vinyl chloride concentration.

9.3.1 Calculate the vinyl chloride concentration as $mg/m^3$. From the calibration curve described in Section 8.4, above, select the value of $W_{vc}$ that corresponds to $H_c$, the sample peak height.

$$C_{vc} = \frac{W_{vc} V_s}{V_m V_i}$$

$$= \frac{W_{vc}}{V_m} \times 10^4,$$

where

$C_{vc}$ = The concentration of vinyl chloride in the air sample, $mg/m^3$.

$W_{vc}$ = The quantity of vinyl chloride measured by gas chromatography, mg.

$V_s$ = The total volume of carbon disulfide in which the vinyl chloride sample is contained, 25 ml.

$V_m$ = The uncorrected sample volume, from 9.1 above, $m^3$.

$V_i$ = The volume of carbon disulfide solution injected into the chromatograph for analysis, 0.0025 ml.

9.3.2 If desired, the concentration of vinyl chloride may be calculated as parts per million vinyl chloride,

ppm VC = mg $VC/m^3$ x 0.3915.

10. Effects of storage. Charcoal tubes containing adsorbed vinyl chloride have been found to be stable for more than seven days though there is some evidence that they are adversely affected by strong sunlight. Carbon disulfide solutions lose vinyl chloride to the atmosphere but have been stored unchanged for more than a month in sealed serum bottles having

minimum headspace. Gas standards may be kept in poly (vinyl fluoride) gas sample bags for several weeks without undergoing concentration changes. However, present knowledge of the stability of vinyl chloride samples is based on studies with pure substances. No information is available on the storage of samples containing other active substances as are commonly found in ambient air.

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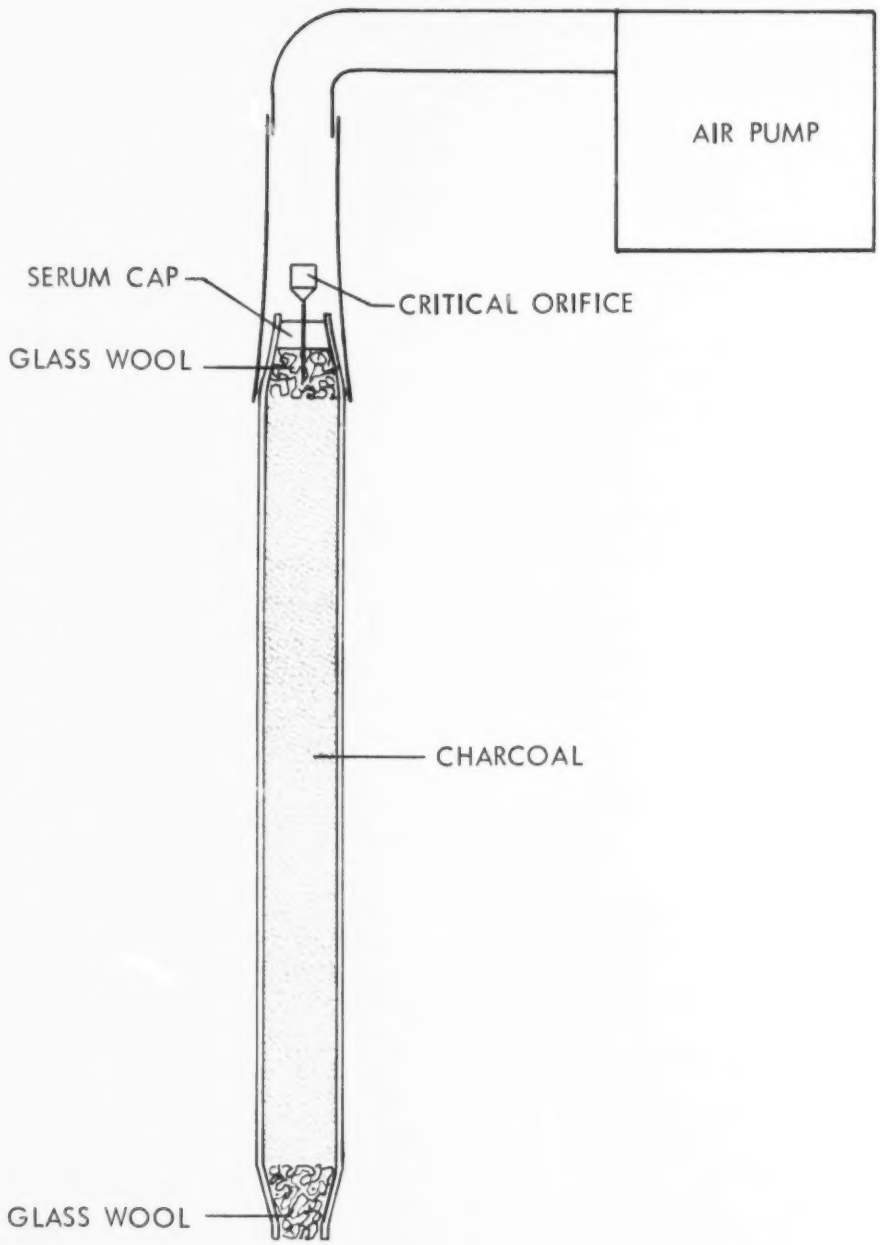
AIR PUMP
SERUM CAP
CRITICAL ORIFICE
GLASS WOOL
CHARCOAL
GLASS WOOL